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GB 1525989 GB 1242009

(58) Field of search

G1A

(54) Probe for measurement of
metal ion concentration

(57) A probe for the colourmetric monitoring of the concentration of a dissolved component in solution that imparts a colour to the solution, e.g. a dissolved metallic component, comprises a light source, means to convert light to an electric signal and two elongate optical elements (2), preferably in the form of single glass fibre canes, one of the optical elements having its upper end in optical communication with the light source and the other optical element having its upper end in optical communication with the converting means; the lower ends (4) of the optical elements being in spaced apart cylindrical alignment with each other. The probe may be mounted on a tank containing the solution to be monitored with the lower ends of the optical elements immersed in the solution, the electrical signal generated by the probe being used to control the operation of a pump for supplying, for example, replenishment concentrate or diluent to the tank.

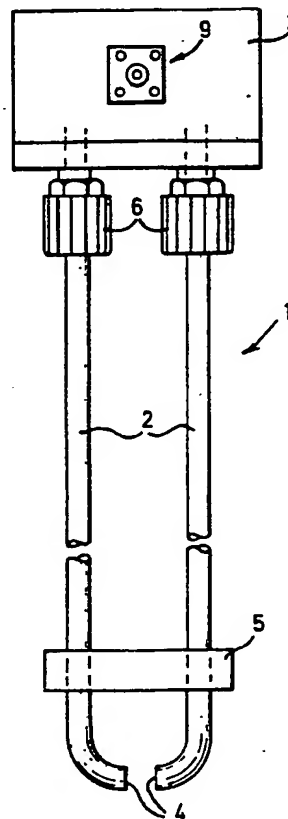


FIG.1.

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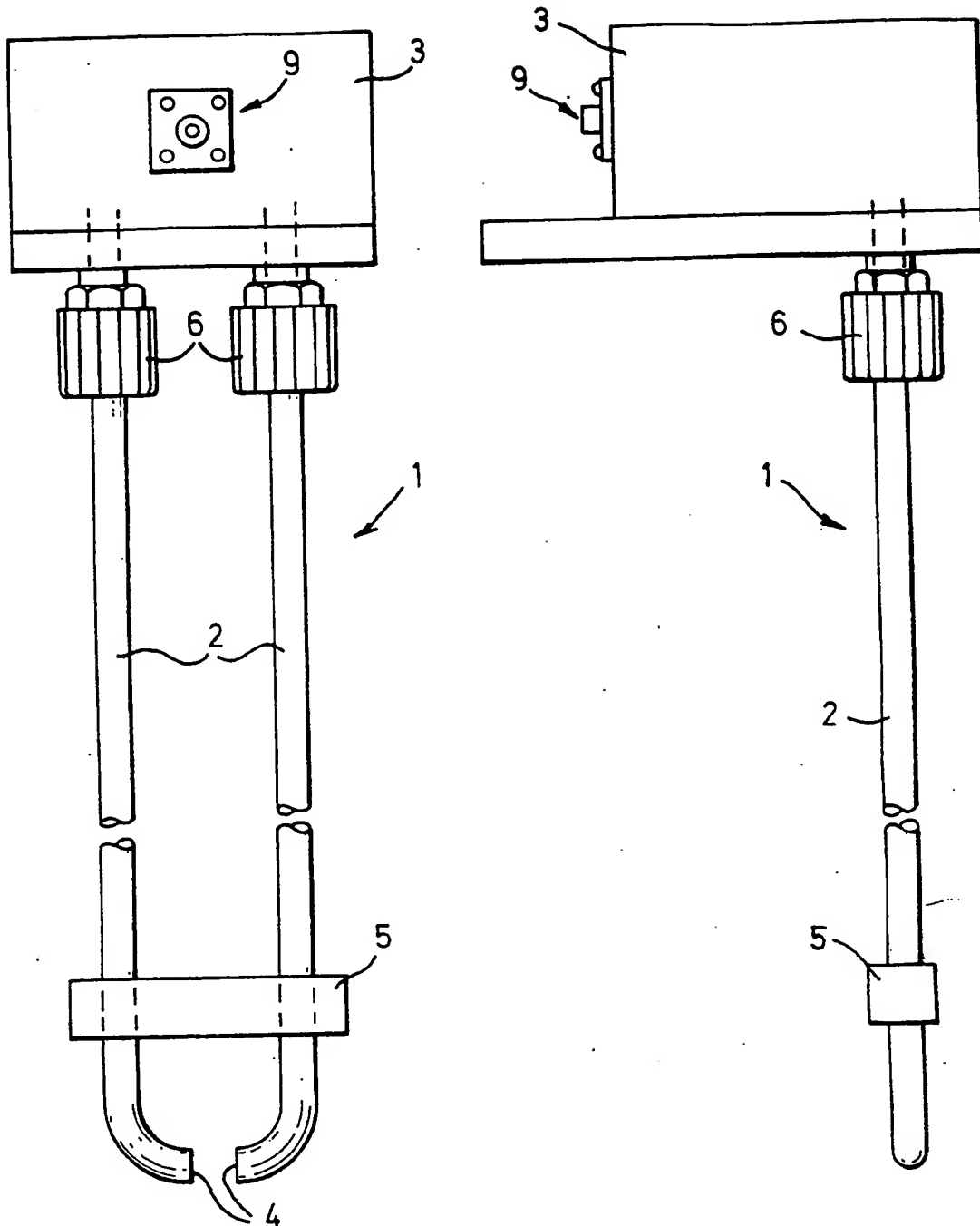


FIG. 1.

FIG. 2.

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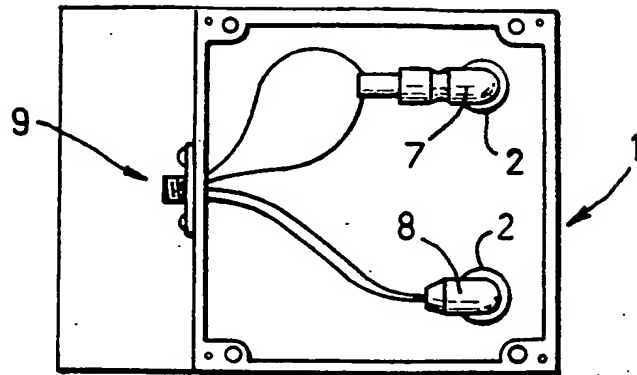


FIG. 3.

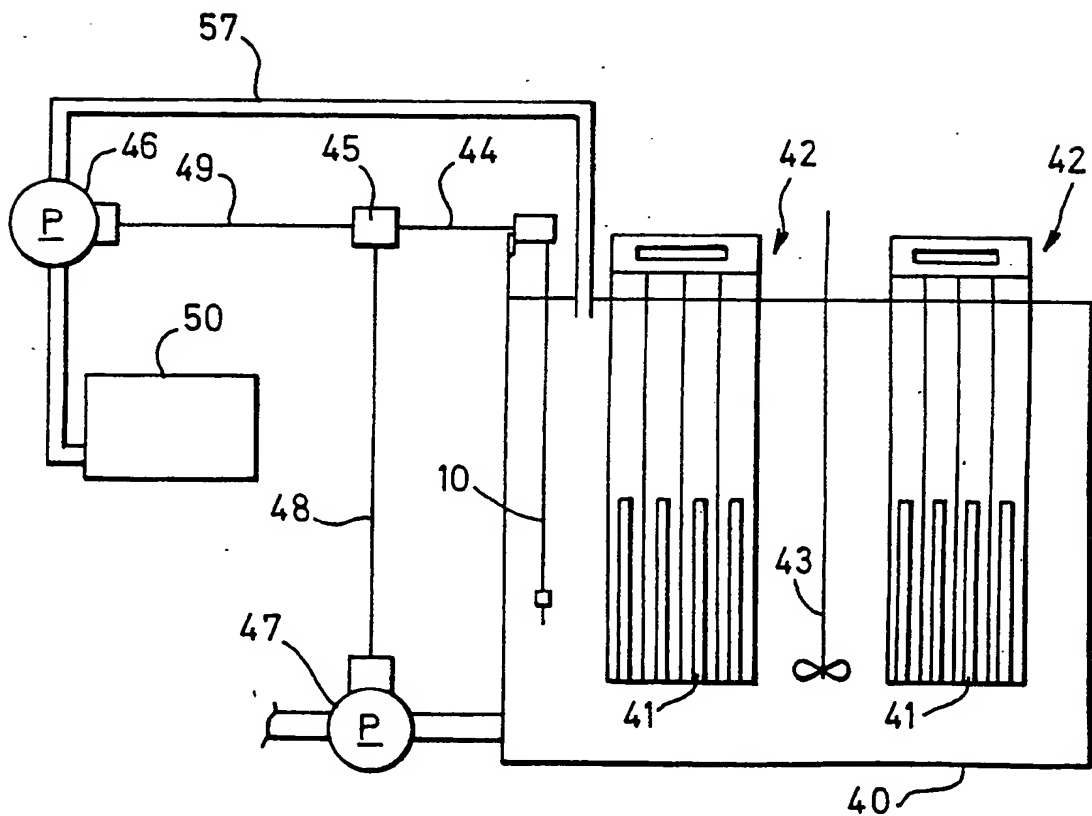


FIG. 4.

SPECIFICATION

Probe for measurement of metal ion concentration

- 5 This invention relates to a probe for measuring the concentration of a dissolved metal in solution and more particularly, to a probe capable of immersion directly into a solution containing a dissolved metal. 5
- Many solutions contain dissolved metals which vary in concentration during the use of solution. For such solutions, it is often desirable or necessary to periodically or continuously
- 10 determine the concentration of the dissolved metal undergoing concentration change. For example, when the concentration of a dissolved metal undergoing concentration change reaches a predetermined level, there may be a need to replenish or remove a portion of the metal content so that its concentration is returned to its approximate initial level. The need for replenishment is especially true with metal plating solutions, typically electroless metal plating solutions such as
- 15 those described in United States Patents Nos. 3,728,137 (for electroless copper) and 3,719,508 (for electroless nickel). For such solutions, as the plating metal is consumed by deposition over a substrate, as the plating metal is consumed by deposition over a substrate, the properties of the solution are altered such as by a decrease in the plating rate and a change in deposit properties. To avoid such changes, these solutions are periodically replenished whereby
- 20 consumable ingredients, such as the plating metal, are returned to their initial concentration levels. For solutions used to etch metal, for example, such as the disclosed in United States Patent No. 3,650,957 (for etching copper), when the concentration of the etched metal builds to an undesirably high level, the etch rate may decrease and undesired deposits may form on the etched surface. To prevent these changes in the properties of the etchants, it is desirable to
- 25 periodically remove a portion of the etched metal by methods known to the art. 25
- Using metal plating solutions for purposes of illustration, it is known that the concentration of the components of such solutions may be periodically monitored by chemical analysis, and in some cases, by continuous analysis using sophisticated analytic instrumentation as described in United States Patents Nos. 3,532,519; 3,951,602; 4,002,786; and 4,096,301. Typically, the
- 30 monitoring equipment is remote from the plating solution because such solutions are corrosive and attack the instrumentation. Consequently, a sample of the solution is typically removed from the plating solution and pumped to a point remote from the solution for analysis. This is undesirable for many applications because the solutions monitored are inherently unstable and when removed from solution in small amounts are subject to oxidation and tend to plate out
- 35 metal from solution in an uncontrolled manner resulting in metal deposition on the probes and on all surfaces upon which they come into contact. This makes accurate measurement of solution components extremely difficult, often impossible. In addition, there is a time lag due to removal of the solution from the tank and also, the sample removed may not be representative of the total solution within the plating tank. 35
- 40 In United States Patent Application Serial No. 169,129 filed July 15, 1980, there is disclosed a probe for colourimetrically detecting the concentration of a dissolved metal in a plating solution. The probe is one that is immersed in a solution containing a dissolved metal. The probe is in the form of a rigid transparent block having an open ended groove of rectangular cross-section at its lower end, which groove defines an elongated passage. At
- 45 opposite ends of the elongated passage, there are spaced parallel walls having a sensor embedded in one wall and a light source embedded in the opposite wall in alignment with the sensor. Electrical conductors are connected respectively to the sensor and light bulb which are also embedded in the rigid block and extend therefrom to a flexible conduit upwardly from the unit and out of the top of the tank. The probe is mounted on a reciprocating rack whereby
- 50 movement of the rack causes solution to flow through the elongated passage and between the sensor and light bulb, where the sensor detects the intensity of the light passing from the bulb to the sensor. This change is passed via the conduit to a control device which may cause removal of a portion of the solution or replenishment of the solution with solution components. 50
- The above described probe is an inexpensive, easily operated device within the plating
- 55 solution permitting simple control of the dissolved metal content of the solution. However, the solutions containing the dissolved metal are corrosive and it has been found that with prolonged use of the probe described in said application, there is eventually some leakage and attack of the corrosion liquid on the metallic parts of the probe. 55
- The present invention provides a probe for the colourimetric determination of a dissolved
- 60 metal in solution that imparts a colour to the solution which probe may be capable of being placed directly within a plating tank in which the solution is contained without risk of corrosive attack. 60
- The probe comprises two elongate optical elements having their lower ends mounted in a spaced apart relationship in optical alignment with each other, whereby solution can pass
- 65 between the ends of the elements. The upper end of one of the optical elements is adjacent a 65

light source while the other element has its upper end adjacent a cell capable of converting changes in light energy to changes in electrical energy, such as a photovoltaic cell. In use, the lower portions of the optical elements of the probe are immersed in the solution containing the dissolved metal while the upper ends of the optical elements are above the liquid level. Light is passed down one element, through the metal containing solution and into the second optical element where it is passed to the photovoltaic cell and converted to an electrical signal. As the concentration of the dissolved metal in solution changes, the optical density of the solution changes since it is the complexed metal content of the solution that imparts colour to the solution in direct correlation to its concentration. A change in the optical density of the solution will result in a concomitant change in the intensity of light passed from one optical element to the other and consequently, a change in the voltage produced by the photovoltaic cell. This change in voltage may be used to activate pumping means to add metal to the solution by replenishment with a concentrated solution of the dissolved metal or, alternatively, to replace a portion of the solution with a diluent to decrease the dissolved metal content.

In a preferred embodiment of the invention, the optical elements comprising the probe are relatively thick, single optical canes drawn from an appropriate billet. This embodiment is preferred over the use of the more conventional thin strand fibre optic bundle as it has been found that there is a tendency for the solution to leak into and "wick" up a fibre optic bundle resulting in corrosion and damage to the probe.

For purposes of illustration, a typical solution that may have its metal content monitored in accordance with this invention is an electroless metal copper plating solution having the following formulation:

| | | |
|---------------------------------|------------|--|
| Copper sulphate pentahydrate | 10 gm | |
| Tartaric acid | 12 gm | |
| Paraformaldehyde | 7 gm | |
| Sodium cyanide | 0.005 gm | |
| Sodium hydroxide (20% solution) | 35 ml | |
| Water | to 1 litre | |

In use of the above copper plating solution, complexed copper—the coloured component in solution, is consumed by plate-out, and, accordingly, decreases in concentration with use. The reduction in concentration of the copper complex does not appreciably change the spectrum of light passing through the solution, but, rather, the optical density of the solution and, hence, the quantity of light that will pass through the solution—i.e., the intensity of the light passed through the solution. This means that more light at all wave lengths is transmitted through the solutions as the copper contained in solution is decreased in concentration. As the concentration of the copper approaches zero, the perceived colour of the solution approaches water white. In summary, the solution would have an intense royal blue appearance at 100% copper concentration and would continue to appear blue as copper becomes depleted, but the intensity of the blue colouration would be reduced until almost all of the copper was plated from solution and consequently, more light at all wave lengths would pass through the solution of the low copper concentration. The difference in the intensity of the light passing through the solution can be read by a colourimeter.

In the following description reference will be made to the accompanying drawings in which:
Figure 1 is a front view of an in-tank probe in accordance with a preferred embodiment of the invention;

Figure 2 is a side view of the probe shown in Fig. 1;

Figure 3 is a top view of the probe shown in Fig. 1 with a top plate removed to display various components of the probe; and

Figure 4 diagrammatically shows a plating tank and control system using the probe of the invention.

As shown Figures in 1–3 of the drawings, the in-tank probe 1 comprises a pair of single strand optical canes 2 and a box or housing 3 containing the electrical components of the probe. The glass canes 2 are relatively thick materials preferably having a diameter of from 1/8 to 3/4 inch (3.175–19.05 mm), and more preferably, a diameter of from 3/8 to 5/8 inches (9.525 to 15.875 mm). The strands are preferably drawn from a thicker billet which itself is encased in a leaded glass tube. The billet encased in the tube is heated to its melting point and drawn to the desired diameter. The leaded glass tube thus sheaths the fibre optic cane in a coating of leaded glass whereby loss of light through the sides of the canes is minimized. The lower extremities of the fibres canes are bent through an angle of 90° and have flat end portions 4 spaced apart and aligned with each other. The space between the end portions is conveniently set at from 1/8 to 2 inches (3.175 to 50.8 mm). The canes 2 are maintained rigidly in position by a brace 5 located near their lower ends.

The optical fibre canes 2 extend upwardly where they are joined to and pass into housing 3.

The canes 2 are preferably secured to housing 3, by a reduction coupling 6 that seals the space between the coupling and the cane to prevent the migration of corrosive liquid into housing 3. Within housing 3, there is positioned a light source 7 in optical communication with one of the glass fibre canes and a photovoltaic cell 8 in optical communication with the other of the glass fibre canes. An alternatives to a photovoltaic cell, there may be used a photoresistive or photoconductive device, all as known in the prior art. The light source and photovoltaic cell are electrically connected to a connector 9 for electrical connection to suitable equipment (not shown) for altering the concentration of a dissolved metal component.

In use, the probe is mounted on a tank containing the solution in which the metal is dissolved. Approximately the lower two-thirds of the glass canes extend beneath the liquid level and the agitated solution passes between the ends 4 of the fibre optic canes 2. Light from light source 7 passes down one of the canes, out of its end, through the solution disposed between the ends of the canes and into the other of the two fibre optic canes where it is passed up to photovoltaic cell 8 and converted to an electrical signal. As the intensity of colour of the solution between the canes change, more or less light passes from one cane to the other resulting in a change in the electrical signal from photovoltaic cell 8. This change, using a suitable controller mechanism such as a simple wheatstone bridge which compares the voltage to a reference voltage, can activate pumping means (not shown) which adds replenisher to the solution or removes solution replacing the same with diluent.

Fig. 4 represents a typical plating tank in combination with a control system containing the probe of the invention. A plating solution, such as the electroless copper plating solution described above, is contained within plating tank 40. The plating solution possesses a dark blue colour because of a complex formed between the dissolved copper and the tartaric acid. Parts to be placed, 41, are held on plating racks 42. Contact of the plating solution with parts properly catalyzed to initiate plating causes metal to deposit on the parts suspended in the solution. The solution is agitated with agitator 43 to ensure solution uniformity throughout the plating tank. As metal is deposited on parts 41, the intensity of the blue colouration decreases because copper is removed from the plating solution.

Probe 10 is suspended in plating tank 40 in a suitable location to permit plating solution to pass between the spaced apart and aligned ends of the probe. Light passes through one fibre optic element of the probe, through the solution and up into the other fibre optic probe. The amount of light passing through the solution is in proportion to the colour of the solution and changes as metal is plated out of the solution. The photovoltaic cell within the probe measures the change in the amount of light passing from one fibre optic to cane to the other. This is converted to a changing electrical voltage by the photovoltaic cell contained within the probe. The electrical signal generated in probe 10 is conducted by electrical conduit 44 to a control device 45, conventional in the art, which may be preset to activate pumping means 46 and/or 47 through electrical conduits 48 and 49. The control device may be programme to activate pumps 46 and 47 when the concentration of copper drops to a predetermined level, typical no less than 90% of its initial concentration, and to shut down when the copper concentration is returned to a predetermined level, such as approximately 100% of its initial concentration.

Replenisher solution is contained within tank 50. This solution may be a concentrated form of the solution contained within tank 40 but is preferably a concentrated solution of complex copper. As pump 46 is activated, replenisher solution is drawn from tank 50, through conduit 51 and into tank 40. In some cases, it may be necessary to withdraw a portion of the plating solution from tank 40 to provide room for the replenisher solution. In such case, pump 47 would be activated at the same time as pump 46 whereby depleted solution is withdrawn from tank 40 and stored or waste treated for disposal.

If an etchant were contained in tank 40 rather than a plating solution, the probe 10 would still be used in similar fashion. As the concentration of dissolved metal in solution increased to an unacceptable level, control means 45 would activate pumps 46 and 47. However, rather than a replenisher solution in tank 50, a diluent or fresh recycled etchant would be contained in tank 50 which would replace removed solution, thus lowering the metal constant in the dissolved solution.

The invention has been described in terms of use of the probe of the invention for the monitoring of the concentration of a dissolved metallic species in solution that changes with use of the solution. It should be understood that the probe of the invention is useful for the monitoring of any dissolved species that imparts a colour to the solution, which dissolved species changes in concentration as the solution is used.

CLAIMS

1. A probe for the colourmetric monitoring of the concentration of a dissolved component in solution that imparts a colour to the solution, which probe comprises a light source, means to convert light to an electrical signal and two elongated optical elements, one of the optical elements having its upper end in optical communication with the light source and the other of

the optical elements having its upper end in optical communication with the means to convert light to an electrical signal, and the lower ends of the optical elements being in spaces apart optical alignment with each other.

2. A probe as claimed in claim 1 in which each optical element is a single fibre glass cane
5 having a diameter of at least 1/8 inch (3.175 mm). 5
3. A probe as claimed in claim 1 or claim 2 in which the optical elements have a thick coating of leaded glass to prevent light from passing through their sides.
4. A probe as claimed in any one of the preceding claims in which the means to convert light to an electrical signal is selected a photovoltaic cell, a photoresistor or a photoconductor.
- 10 5. A probe as claimed in any one of the preceding claims in which the optical elements each have a rounded 90° bend and the ends of the canes are flat, adjacent each other and separated by a distance of at least 1/8 inch (3.175 mm). 10
6. A probe as claimed in claim 1 substantially as hereinbefore described with reference to Figs. 1-3 of the accompanying drawings.
- 15 7. A probe as claimed in any one of the preceding claims electrically connected to pumping means, which pumping means are activated in response to changes in the electrical signals generated by said probe. 15
8. A probe as claimed in claim 7 in which the pumping means are activated when light passing through the optical elements is increased to a given predetermined level.
- 20 9. A probe as claimed in claim 7 in which the pumping means are activated when light passing through the optical elements is decreased to a given predetermined level. 20
10. A combination comprising a tank containing a solution of a dissolved metal that yields a colour in solution and a colourimetric probe as claimed in any one of claims 1-6, the probe being attached to the tank in a manner whereby the lower ends of the optical elements are
25 beneath the surface and within the solution and the upper ends of the optical elements, the light source and the means to convert light to an electrical signal, are external to the solution. 25
11. A combination as claimed in claim 10 further provided with a second liquid containing tank, pumping means in electrical contact with said probe and piping connecting the pump with the tank and the second tank.
- 30 12. A combination as claimed in claim 11 in which the tank contains a metal plating solution and the second tank contains a concentrated solution of a dissolved metal that is the same metal as the metal of the plating solution. 30
13. A combination as claimed in claim 12 in which the pump is activated when the metal content of the plating solution is reduced to a predetermined level whereby the plating solution
35 is replenished by addition of a concentrated solution of said depleted metal. 35
14. A combination as claimed in claim 11 in which the tank contains an etching solution and the second tank contains a diluent for the etching solution.
15. A combination as claimed in claim 16 in which the pump is activated when the metal content of the etching solution is increased to a predetermined level whereby the plating
40 solution is diluted by addition of a diluent for the etching solution. 40
16. A combination as claimed in claim 11 substantially as hereinbefore described with reference to Fig. 4 of the accompanying drawings.
17. A process for monitoring the concentration of a dissolved metal in solution which solution is within a container and which dissolved metal imparts a colour to the solution and
45 changes in concentration during use of the solution, which process comprises immersing a colourimetric probe as claimed in any one of claims 1-6 directly into the solution within the container and passing light through the optical elements whereby changes in optical density of the solution that occur as a consequence of a change in the concentration of the dissolved metal will be converted to an electrical signal. 45
- 50 18. A process as claimed in claim 17 in which pumping means are activated in response to changes in the electrical signals generated by the probe. 50
19. A process as claimed in claim 18 in which the pumping means are activated when light passing through the optical elements is decreased to a given predetermined level.
20. A process as claimed in claim 18 in which the pumping means are activated when light
55 passing through the optical elements is increased to a given predetermined level. 55
21. A process as claimed in claim 17 substantially as hereinbefore described.